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Transition-metal control of electronic and magnetic properties in GeC semiconductor: spin density functional calculations

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Abstract

The electronic structures and magnetic properties of GeC doped with several transition metals are presented by the spin density functional theory. Transition metals are energetically favorable to substitute in Ge lattice site. Through the band structures, transition metals doping in GeC lead to a spin polarization. The main contributions to the net magnetization mainly originate from transition metal, C and Ge atoms, respectively. The magnetism produced by transition metal is occurred from the hybridization of d states of the transition metal with C-p states, called p–d exchange hybridization. (Ge, Cr)C is characterized as the semiconductor with a reduced band gap. Co, Cu and Fe doping in GeC are classified as metal. The emergence of half-metallic characteristics is in (Ge, Mn)C displaying the dilute magnetic semiconductor which can be implemented for the spintronic applications. Finally, this is the first theoretical prediction to investigate the electronic and magnetic properties of transition-metal doped GeC compound and still waits for the experimental confirmations.

Keywords: transition metal, GeC, spin density functional calculations, magnetism, electronic properties

(Some figures may appear in colour only in the online journal)

Introduction

Germanium carbide (GeC) is one of Group IV alloying compounds that has been appealed for the extensive applications in optoelectronic devices because of its narrow optical band gap [1–8] and in photovoltaics and infrared optical devices due to low stress, tuned refractive index, high absorption coefficient, tunable band gap and good combination on infrared substrates (ZnS, Si and Ge) [9–16]. Experimental and theoretical calculations in GeC semiconductor have been investigated expansively [17–36]. Recently, there are several theoretical investigations of GeC semiconductor with zinc-blende phase, while the experimental confirmations remain undiscovered. To manipulate the natural properties for the extensive applications, doping technique has been reported to be an effective way to modify the host properties and has been demonstrated widely. For instance, Ameri *et al* [7] studied the electronic properties of $Si_xGe_{1-x}C$ compound by FP-LMTO method. The physical properties depended upon the concentration. A density functional theory was used to scrutinize the electronic and optical properties of $GeC_{1-x}B_x$ in zinc-blende phase as a function of B concentrations by Che *et al* [37]. The transformation from indirect band gap to direct band gap in GeC was arisen in the presence of B atom. Rostami *et al* [38] presented the physical properties of Cr-doped SiC, GeC and SnC using mBJ-GGA approximation. The half-metallic ferromagnets were achieved. As the results of Zhai *et al* [39], the effect of germanium content on the electronic properties of $Si_{1-x}Ge_xC$ alloys was investigated by the first principles calculations. Ge doping changed the symmetry of SiC and delivered the indirect to direct band gap transition. Xu *et al* [40–42] reported the calculations of the structural, electronic and optical properties in zinc-blende GeC semiconductor, nanoribbons and monolayers doped with

B, N and Ni by the first-principles calculations. The impurities changed the magnetic moment and announced the magnetism inside these systems. Manikandan *et al* [43] investigated the electronic properties of $Si_{1-x}Ge_xC$ with the increasing Ge contents using first principles calculations. The band gap of SiC was increased in the presence of the Ge doping. Shakerzadeh [44] studied the effect of carbon and silicon impurities on the structural and electronic properties of $(GeC)_{12}$ nanocluster under the applied electric field by the density functional theory. The natural properties of these nanocluster were not noticeably changed with the increasing electric field strength but these clusters were stable for the all range of the applied electric fields. Behzad [45] investigated the structural, electronic and optical properties of Si atoms substituted in GeC monolayer by density functional theory. The atomistic computations of GeC monolayer were mainly sensitive with the number of Si atoms. Sharma *et al* [46] characterized 2D $Si_{1-x}GeC_x$ alloys by density functional theory using the hybrid functional of Heyd–Scuseria–Ernzerhof. The computations of the electronic structures, thermodynamical stability and optical properties depended on the compositions (x). Gökçe *et al* [47] studied the adsorption of C, Si and Ge on GeC honeycomb structure by the generalized gradient approximation (GGA). The adsorption of Si and Ge demonstrated the n-type doping, while C atom convinced the p-type doping. Xu *et al* [48] analyzed the electronic and thermodynamic properties of a honeycomb $Si_{1-x}Ge_xC$ monolayer by first-principles calculations. The band gaps were reduced with the increasing concentrations (x).

As the results of the abovementioned literature, only a few works were accomplished in electronic structures and magnetic properties of GeC semiconductor by the substitution of transition metals. This scientific work accumulates into one place the correlated pieces of information related to the structural, electronic and magnetic properties of GeC semiconductor doped with Cr, Mn, Fe, Co and Cu with the concentrations of 12.5%. The favorable replacing sites of transition metals doping at Ge or C site in GeC semiconductor are energetically scrutinized. The emergence of half-metallic behavior by changing the transition metals doping in GeC semiconductor is also exploited. The half-metallic behavior in transition-metal doped GeC semiconductor can be implemented for the spintronic applications. Spintronics, spin electronics, is the utilization of an intrinsic spin property of electron for the data processing. Exploitation of spin properties and charge degrees of freedom efficiently provides the electronic devices with a greater miscellany of functionality. In addition, the control of electronic and magnetic properties in GeC semiconductors by transition metals unlocks a new track for the transition-metal GeC-based electronic devices. A knowledge of the electronic and magnetic properties is key issue in promoting these systems for device applications. Utilizing the GGA with the Perdew–Burke–Ernzerhof (PBE) exchange functional [49] in the CASTEP package [50, 51], GeC semiconductors doped with different transition metals are determined. This computational work can support and deliver the exploration of transition-metal doped GeC compounds as the novel spintronic materials. For the presentation of this paper, section 2 describes the computational methodology utilized in this work. The theoretical results and a discussion of each configuration concerning the lattice parameters, volumes, total energies, formation energies, band gaps, magnetizations, spin-polarized band structures, density of states and partial density of states are analyzed and presented in section 3. Finally, a conclusion is demonstrated.

Theory

The electronic structures and magnetic properties of GeC semiconductor doped with several transition metals are computed by the spin-polarized density functional theory as accomplished in CASTEP package. The exchange-correlation effects are estimated under the GGA parameterized by PBE. The lowest probable cut-off energy for the plane wave basis set is achieved by the ultrasoft pseudopotentials announced by Vanderbilt. For the expansion of the plane wave function basis, the energy cutoff of 520 eV is used throughout this paper. The Brillouin zone integration is performed over $4 \times 4 \times 4$ grid sizes using the Monkhorst–Pack method. According to the literature data from Wei *et al* [52], the experimental dopant concentration from 5% to 30% was obtained in the compounds with zinc-blende phase. Here, GeC semiconductor displaying the zinc-blende structure with a space group of F-43m is a model for the simulations. Before the study of transition metal doping, the structural calculations of bulk GeC semiconductor need to be confirmed first to obtain the precision of the computational method. The lattice constant of GeC is 4.604 Å which is in a good agreement with the former results (4.59 Å [36], 4.589 Å [34], 4.61 Å [27], 4.54 Å [30], 4.62 Å [26], 4.43 Å [31], 4.49 Å [53] and 4.53 Å [54]). The GeC band gap with 1.602 eV agrees well with the earlier data (1.625 eV [35], 1.54 eV [25], 2.46 eV [27], 1.650 eV [28] and 1.52 eV [30]). Therefore, this technique is suitable to study the electronic and magnetic properties of GeC semiconductor with Ge or C substitution by transition metals like Cr, Mn, Fe, Co and Cu. In order to explore the electronic structures and magnetic properties of transition-metal doped GeC compound, I employ a $2 \times 1 \times 1$ supercell containing 16 atoms and use the substitutional method to set the doped method. A $2 \times 1 \times 1$ supercell of GeC semiconductor is presented in figure 1. The doped GeC system is constructed by replacing a Ge or C atom by a transition metal in a supercell. The magnetic configuration is ferromagnetic. In the presence of the doped transition metals, the structures are fully optimized by the Broyden–Fletcher–Goldfarb–Shanno minimization algorithm [55–58]. The convergence criterions of the total energy, maximum force, maximum stress and maximum displacement are 2.0×10^{-6} eV/atom, 1.0×10^{-5} eV Å^{-1}, 0.05 GPa and 0.001 Å, respectively. Finally, the structural, electronic and magnetic properties of all configurations are evaluated from lattice parameters, volumes, total energies, formation energies, band gaps, magnetizations, electronic band structures, density of states and partial density of states. According to none of available experimental data, the comparison is not attained.

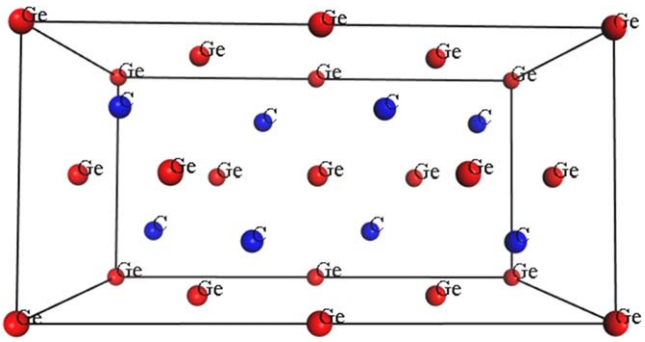

Figure 1. The crystal structure of 2 × 1 × 1 GeC supercell in zinc-blende phase.

Table 1. The calculated total energies and formation energies of GeC with Ge and C substitution by Cr, Mn, Fe, Co and Cu.

	Total energy (eV)	Formation energy (eV)
GeC	−2092.92	—
(Ge, Cr)C	−4451.32	−4.241
Ge(C, Cr)	−4400.68	3.861
(Ge, Mn)C	−2636.03	0.121
Ge(C, Mn)	−2588.02	5.597
(Ge, Fe)C	−2848.40	−3.506
Ge(C, Fe)	−2798.64	3.715
(Ge, Co)C	−3025.72	−1.524
Ge(C, Co)	−2977.04	4.620
(Ge, Cu)C	−3458.52	4.776
Ge(C, Cu)	−3411.24	9.516

Results and discussions

The main purpose is to comprehensively understand the effect of transition metal doping on the structural, electronic and magnetic properties of GeC semiconductor using the GGA with the PBE exchange functional. It is hopeful that this work may promote the exploration of transition-metal doped GeC compound as new spintronic and optoelectronic materials in the future. First, the energetically preferable replacing positions of transition metals doping at either Ge or C site in GeC semiconductor are studied by calculating the total energies and formation energies as listed in table 1. The formation energies of the transition metals doping at either Ge or C site in GeC semiconductor are described in more detail in [40]. The total energies and formation energies of GeC with the substitution of Ge by transition metals are lower than those of GeC with the substitution of C by transition metals. Hence, the results underline that substitutions of all transition metals in Ge lattice site are energetically more favorable than those in C site. Due to the formation energies, (Ge, Cr)C is the most stable among all doped compounds. Keeping this in mind, the structures with substitution of transition metal in Ge lattice site are utilized as the modeling. Table 1 enumerates the computed lattice parameters and their volumes at equilibrium. The transition metals doping in GeC semiconductor induce the changes in the structural properties because of the difference of radius between impurities and host. With the incorporation of transition metals, lattice a are increased but lattice *b* and *c* are reduced. This is due to the fact that the non-cubic supercell of GeC semiconductor creates an artificial anisotropy of the stress. (Ge, Mn)C possesses the highest volume among the other doped compounds. The band gaps of GeC compounds doped with various transition metals are also enumerated in table 2. To best of my knowledge, there is no theoretical or experimental data concerning the band gaps. Cr doping in GeC is characterized as a semiconductor with a reduced band gap, while the others are metal. To get detailed knowledge about the origins of the magnetism, the total and local magnetic moments from transition metal, adjacent Ge and nearest C are summarized in table 2. The main contributions to the net magnetization mainly derive from transition metal, C and Ge atoms, respectively. It is observed that C atom connecting to the transition metal mainly obtains the magnetic moment from transition metal dopants. The high-to-low values of the local magnetic moments are found in (Ge, Mn)C, (Ge, Fe)C, (Ge, Cr)C, (Ge, Co)C and (Ge, Cu)C, respectively. Here, it is difficult to compare with experimental findings because there is no available experimental data. To observe the electronic properties, the spin-polarized band structure of undoped GeC semiconductor is schemed in figure 2 under different spin directions and drawn along the symmetry paths in the involved Brillouin zone. There is no spin polarization between the alpha and beta spin channel, representing the semiconducting behavior. When transition metals are doped in GeC semiconductor, the spin-resolved band structures are depicted in figure 3 along the high symmetric directions in the first Brillouin zone. The substitution of transition metals in GeC leads to a spin polarization for alpha and beta component, thus showing the magnetism inside these structures. (Ge, Cr)C is characterized as semiconductor with a decreased band gap. Mn doping in GeC compound provides the half metallic character because of alpha being metal and beta being semiconductor. In addition, the metallic nature is observed in (Ge, Co)C, (Ge, Cu)C and (Ge, Fe)C because there is the Fermi level running through the conduction and valence bands. Through the band structure calculations, these findings suggest that Mn doping in GeC semiconductor is the promising dilute magnetic semiconductor which can be implemented for the spintronic applications.

In the following paragraph, more details about the electronic properties of GeC semiconductor doped with different transition metals near the Fermi level are acquired by means of total and partial density of states. The total and partial density of states of pure GeC and transition-metal doped GeC are illustrated in figure 4. The up spin and down spin channel of GeC are symmetric. Notice that the non-overlapping valence and conduction states highlight that GeC exhibits semiconducting performance. The conduction bands nearby the edge are mainly derived from Ge-p states. However, in the region with the energy greater 4.0 eV the mixture of Ge-p and C-p states is predominantly dominated. The valence bands are mainly originated from p orbital of C atoms. When doping with transition metals, the spin polarization in both spin channels appears. The transition metals doping in GeC

Table 2. The calculated lattice parameters, volumes, band gaps and magnetic moments of GeC with Ge substitution by transition metals (TM).

	GeC	(Ge, Cr)C	(Ge, Mn)C	(Ge, Fe)C	(Ge, Co)C	(Ge, Cu)C
a (Å)	9.208	9.226	9.387	9.223	9.235	9.228
b (Å)	4.604	4.589	4.574	4.571	4.562	4.577
c (Å)	4.604	4.589	4.574	4.571	4.560	4.577
Volume (Å^3)	195.200	194.290	196.390	192.706	192.197	193.317
Band gap (eV)	1.602	0.473	0.000	0.000	0.000	0.000
$M_{tot}(\mu_B)$	0.000	3.459	5.027	4.043	3.011	1.033
$M_{Ge}(\mu_B)$	0.000	0.0300	0.010	0.030	0.020	0.020
$M_C(\mu_B)$	0.000	0.110	0.040	0.060	0.130	0.170
$M_{TM}(\mu_B)$	—	2.960	4.230	3.420	2.160	0.240

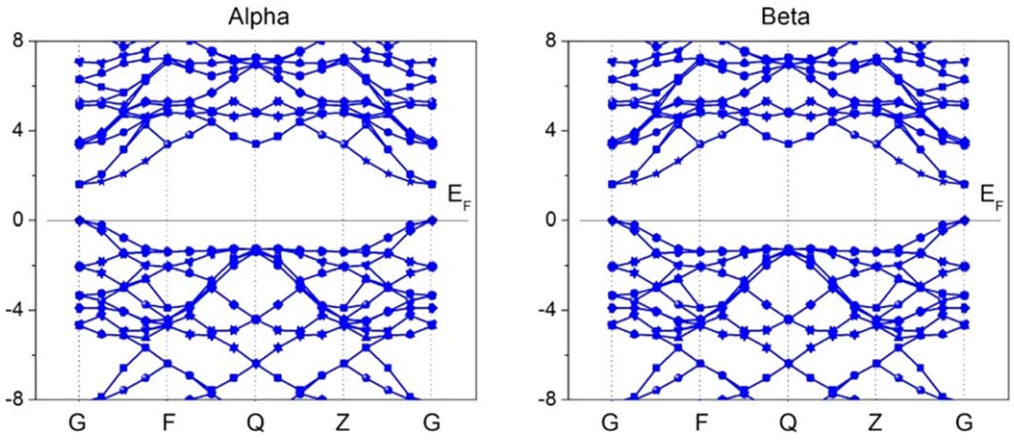

Figure 2. Spin-polarized band structures of pure GeC. Alpha and beta are referred to spin up and spin down, respectively.

semiconductor change the crystal geometry and hybridization of electronic states, leading to some differences in the density of states. The states of the impurity are introduced across or nearby the Fermi level. These states are mainly consisted of the d orbital of the transition metals and p orbital of C. The magnetism is produced from the hybridization of d states of the transition metal with C-p states, named p–d exchange hybridization. Both spin channels in (Ge, Cr)C are fully occupied so (Ge, Cr)C is categorized as the semiconductor with a reduced band gap. In (Ge, Mn)C compound, the up spin channel is metal but the down spin channel is semiconductor. Mn doping in GeC compound becomes half metallic, showing a dilute magnetic semiconducting behavior. The hybridization of Mn-d states with C-p states announces a gap in beta channel with spin polarization of 100% at Fermi energy. Mn doping in GeC provides n-type character due to the high hybridization between p and d orbital near the conduction band edges. So, this transformation as doping with Mn will be a significant advantage in the application of spintronics. The spin channels are partially filled in (Ge, Co)C, (Ge, Cu)C and (Ge, Fe)C compound, presenting the metallic property. Finally, the computations of this work open a spectrum of possible new transition-metal GeC-based electronic devices with their controlled and tuned properties.

Conclusions

A first-principles study based on the density functional theory is carried out to comparatively investigate the electronic structures and magnetic properties of zinc-blende GeC semiconductor doped with various transition metals. The electronic structures and magnetic properties are sensitive with the types of transition metal. The transition metal is the most important source of the net magnetic moment, while C and Ge deliver the minor magnetic moment. The high-to-low values of the local magnetic moments are observed in GeC semiconductor doped with Mn, Fe, Cr, Co and Cu, respectively. Through the partial density of states, the magnetism is formed by p–d hybridization between d orbitals of transition metal and p orbitals of C. Co, Cu and Fe doping in GeC transform semiconductor to metal. (Ge, Cr)C remains the semiconductor with a reduced band gap. Mn doping in GeC semiconductor has half-metallic n-type characteristics, showing the dilute magnetic semiconductor. Overall, I hope that the transition-metal impurity can develop the new implications for GeC semiconductor in the novel applications of magnetic devices.

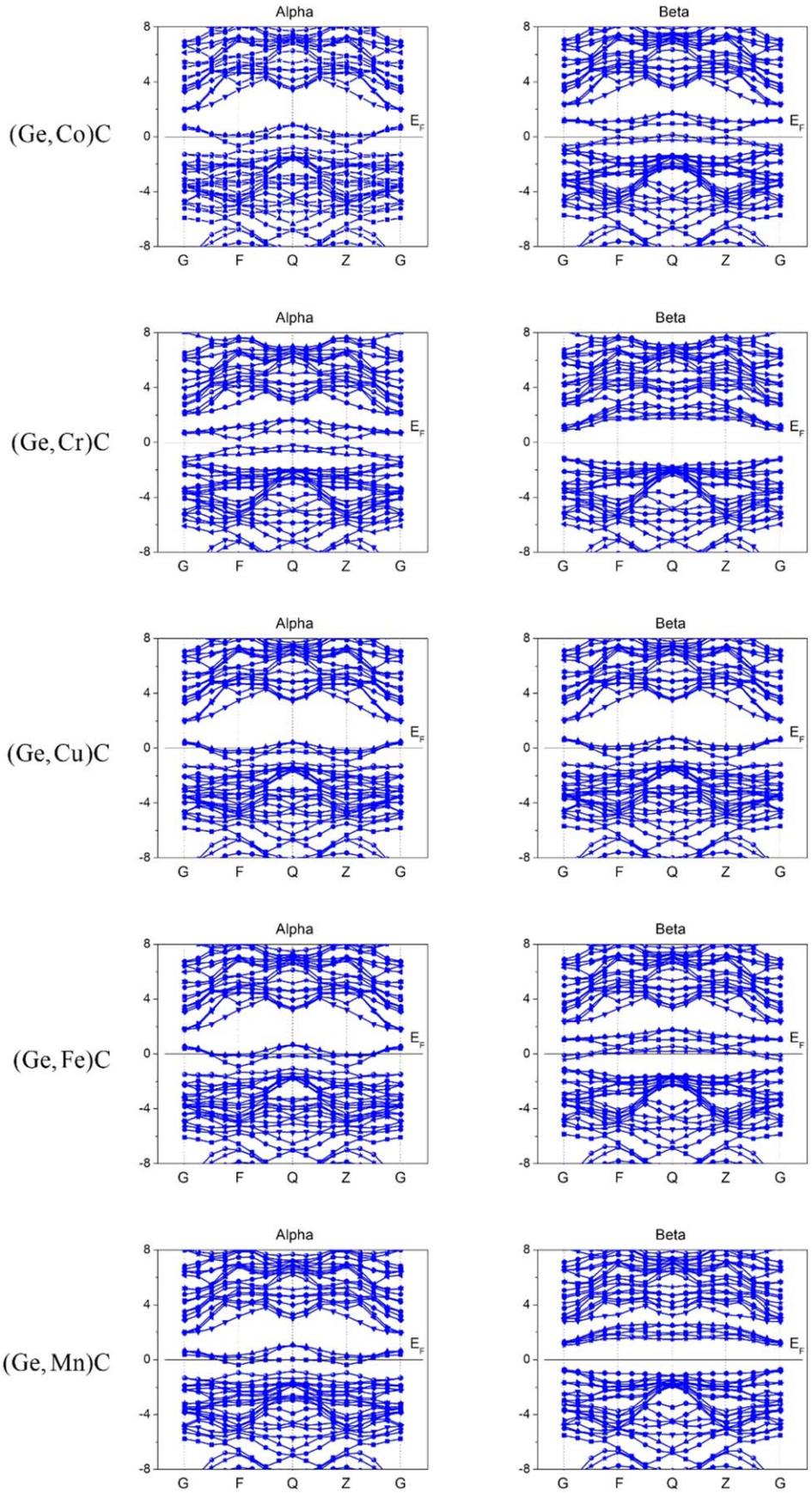

Figure 3. Spin-polarized band structures of (Ge, Cr)C, (Ge, Mn)C, (Ge, Fe)C, (Ge, Co)C and (Ge, Cu)C 2 × 1 × 1 supercell structures. Alpha and beta are referred to spin up and spin down, respectively.

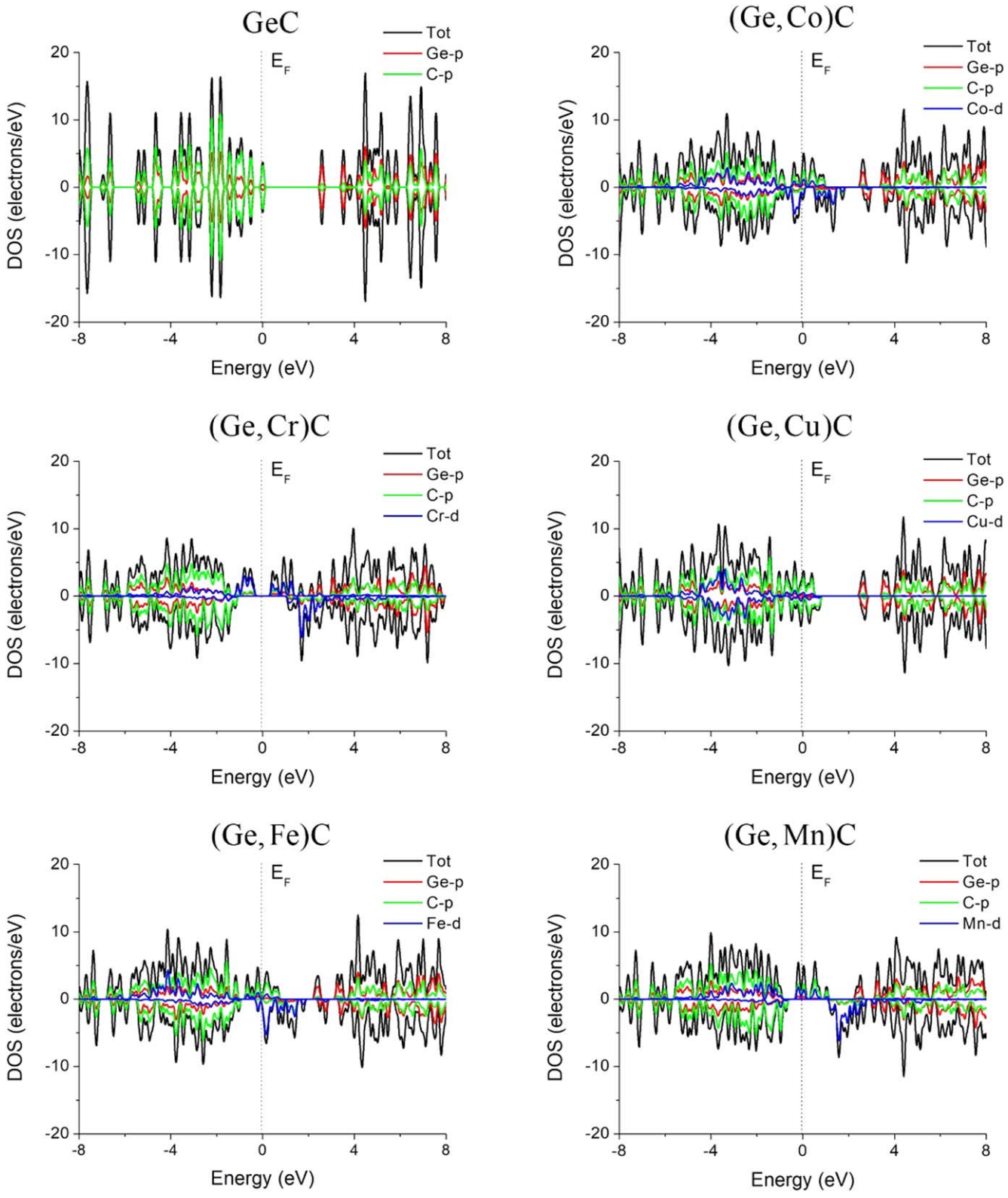

Figure 4. The total and partial density of states of GeC, (Ge, Cr)C, (Ge, Mn)C, (Ge, Fe)C, (Ge, Co)C and (Ge, Cu)C. Positive and negative numbers on DOS axis indicate the up and down spin states, respectively.

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